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REPORT OF INVESTIGATIONS — NO. 66

INVESTIGATION OF THE EFFECT OF HEAT ON THE CLAY MINERALS ILLITE AND MONTMORILLONITE

BY

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ILLUSTRATIONS

INVESTIGATION OF THE EFFECT OF HEAT ON THE CLAY MINERALS ILLITE AND MONTMORILLONITE*

By R. E. Grim and W. F. Bradley

ABSTRACT

Samples of three purified illites, one purified montmorillonite, and one natural clay containing montmorillonite, quartz, and limonite were heated at successive temperatures up to 1400°C. X-ray and optical determinations were made on all samples. The changes that take place in the clay minerals, illite and montmorillonite, when they are heated at various temperatures up to 1400°C. are discussed.

INTRODUCTION

The concept that clays are composed essentially of extremely minute crystalline particles of one or more of a few minerals, known as the clay minerals, is generally accepted by students of clays. It is further recognized that there are only three important groups of clay minerals (Table 1), that is, almost all clays are composed of extremely small particles (frequently less than 0.001 mm. in diameter) of one or more of these three clay mineral groups.

Table 1.—Important Clay Mineral Groups[a]

Name	Chemical composition	Occurrence
Kaolinite	$(OH)_8Al_4Si_4O_{10}$	China clay, fireclay, ball clay, etc.
Illite	$(OH)_4K_y(Al_4 \cdot Fe_4 \cdot Mg_4 \cdot Mg_6)(Si_{8-y} \cdot Al_y)O_{20}$	Shale, fireclay, ball clay, etc.
Montmorillonite	$(OH)_4Al_4Si_8O_{20} \cdot xH_2O$	Bentonite, gumbotil, loess, etc.

[a]For details concerning other clay minerals and possible variations in the composition and properties of clay minerals generally, see R. E. Grim, "Relation of Composition to Properties of Clays," *Jour. Amer. Ceram. Soc.*, **22** [5] 141–51 (1939). Reprinted as Illinois State Geol. Survey Cir. 45.

Considerable study has been made of the changes that take place in kaolinite[1] when it is heated at various elevated temperatures, but no detailed study appears to have been made of the effect of heat on illite and montmorillonite. As montmorillonite and illite are the dominant constituents of many clays, and minor but important constituents of other clays used for ceramic purposes, a knowledge of the effect of heat on these clay minerals is important for an understanding of the firing characteristics of many clays. Further, the firing behavior of clays that are mixtures of clay minerals cannot well be understood until the firing characteristics of the pure clay minerals have been studied. It is the purpose of this report to give the results of an investigation of the changes that take place when illite and montmorillonite are heated at various temperatures up to 1400°C.

PROCEDURE

Samples of illite were purified from two Pennsylvanian underclays and one argillaceous Ordovician dolomite found in Illinois. The crude samples were selected on the basis of previous detailed mineralogical analyses of many argillaceous materials, which showed that these materials contained illite that could be easily separated from the other constituents by a simple sedimentation procedure. The actual purification procedure was as

*Presented at the Forty-Second Annual Meeting, American Ceramic Society, Toronto, Canada, April 9, 1940 (Materials and Equipment Division). Received June 7, 1940.

[1](*a*) T. N. McVay and C. L. Thompson, "X-Ray Investigation of Effect of Heat on China Clays," *Jour. Amer. Ceram. Soc.*, **11** [11] 829–41 (1928).

(*b*) R. A. Heindl and W. L. Pendergast, "Fire Clays, Some Fundamental Properties at Several Temperatures," *ibid.*, **13** [10] 725–50 (1930).

(*c*) J. F. Hyslop, "Chemistry of Fire Brick," *Jour. West Scot. Iron Steel Inst.*, **40** [Part 2] 23–28 (1932).

(*d*) L. Tscheischwili, W. Büssem, and W. Weyl, "Metakaolin," *Ber. deut. keram. Ges.*, **20** [6] 249–76 (1939); *Ceram. Abs.*, **18** [10] 279 (1939).

follows: The clays (including the clay fraction of the dolomite after removal of the carbonate by dilute HCl) were placed in suspension. Ammonium hydroxide was used as the dispersing agent because no salt residue forms when the sample is dried. The suspension was allowed to stand until material coarser than 0.001 mm. had settled out. The suspension remaining was removed and dried on a steam bath. This material, composed of particles finer than 0.001 mm., was shown by X-ray diffraction analyses to contain only illite as the clay mineral. A small amount of quartz that could not be removed in the sedimentation process was also present. Before firing, the dried material was ground to pass a 100-mesh sieve.

It has previously been reported[2] that clay minerals belonging to the illite group may vary somewhat in their physical characteristics and their chemical composition, notably in the K_2O content. One illite sample (No. 1) is representative of illite with relatively high plastic and bonding properties, slightly lower K_2O content, and smaller ultimate particle size. The other illite samples (Nos. 2 and 3) are representatives of illite with relatively larger ultimate particle size and low plastic and bonding properties. The chemical composition and source of the purified illite are given in table 2.

One sample of montmorillonite (No. 4) was purified from a sodium bentonite (pH = 9.04) by the same process used for the illite samples. The purified sample was composed of particles less than 0.001 mm. in diameter, and X-ray diffraction analysis showed the presence of montmorillonite and about 10% of quartz. The other montmorillonite sample (No. 5) was an impure calcium-hydrogen bentonite (pH = 4.10), containing quartz in grains up to 0.1 mm. and limonite in addition to the montmorillonite. This latter sample was not purified.

Small separate portions (about 0.2 gram) of each sample were heated for two hours in platinum crucibles in an electric furnace at 100°, 150°, 200°C., and so on at 50°C. intervals, up to 1100°C. Additional portions of each sample were heated in Alundum crucibles in a gas-fired furnace for two hours at 1200°, 1300°, and 1400°C. In order to determine whether a two-hour firing approached equilibrium conditions, small portions of each sample were fired for six hours at 450°, 600°, and 800°C. No significant changes were apparent for these longer heatings, but the gradual appearance of some features would suggest that true equilibrium may not strictly have been attained. Equilibrium, however, is not critical in these studies. All temperature measurements were made by thermocouples. The heated samples were studied with the petrographic microscope and by means of X-ray diffraction analysis.

Table 2.—Chemical Composition and Source of Samples[a]

Sample (1), purified illite from Pennsylvanian underclay, Grundy County, Ill.; (2), purified illite from Pennsylvanian underclay, Vermilion County, Ill.; (3), purified illite from Ordovician Maquoketa clayey dolomite, Kane County, Ill.; (4), purified montmorillonite from Cretaceous bentonite, Wyo.; and (5) bentonite from Cretaceous, near Pontotoc, Miss.

	Sample No.				
	(1)	(2)	(3)	(4)	(5)
SiO_2	52.79	51.22	51.10	64.60	57.55
Al_2O_3	24.99	25.91	21.96	20.80	19.93
Fe_2O_3	4.68	4.59	6.38	3.05	6.35
FeO	1.10	1.70	1.65	0.46	0.95
MgO	2.70	2.84	3.91	2.30	3.92
CaO	0.09	0.16	1.73	0.53	1.94
Na_2O	0.20	0.17	0.03	2.60	0.33
K_2O	5.86	6.09	6.62	0.40	0.59
TiO_2		0.53	0.46	0.15	0.32
Ignition loss	7.14	7.49	6.24	4.74	8.53
Total	99.55	100.70	100.08	99.63	100.41
H_2O+	6.83	7.14	5.75	4.74	8.51
H_2O-	5.56	1.45	1.74	8.00	7.43

[a]Analyses made under the supervision of O. W. Rees, Chemist, Illinois State Geological Survey.

CHANGES IN PHYSICAL CHARACTERISTICS

Illite

The three samples of illite, before firing, were light gray to light gray-green in color. All of the samples showed the same changes in characteristics up to about 1100°C.; they became very light yellow-red at 250°C., and this color darkened slightly with increased firing tempera-

[2](a) R. E. Grim, "Relation of Composition to Properties of Clays," *Jour. Amer. Ceram. Soc.*, **22** [5] 141–51 (1939); Illinois State Geol. Survey Cir. 45, 1939.
(b) R. E. Grim and W. F. Bradley, "A Unique Clay from the Goose Lake, Ill., Area," *Jour. Amer. Ceram. Soc.*, **22** [5] 157–64 (1939); Illinois State Geol. Survey Report Inv. 53, 1939.

tures up to about 900°C. At 900°C., the samples were red-brown and had a loose powdery character; at 950°C., they retained the same color but had formed aggregates that could be broken with slight pressure. All samples were well vitrified by 1100°C., and they were completely vitrified at 1200°C. Sample (1) at 1300°C., was brown, dense, slightly bloated; at 1400°C., it was a steel-gray glass with many large bloat holes. Sample (2) at 1300°C. was a steel-black glass with many bloat holes which had disappeared at 1400°C. Sample (3) showed a higher degree of vitrification at 1100°C. than samples (1) and (2). At 1200°C., it was a dark brown glass with many small bloat holes which had disappeared at 1300°C. and 1400°C.

It is interesting to note that the illite sample (No. 1) with the high plastic and bonding properties and slightly lower K_2O content is the only one that remained bloated at 1400°C. Sample (3),

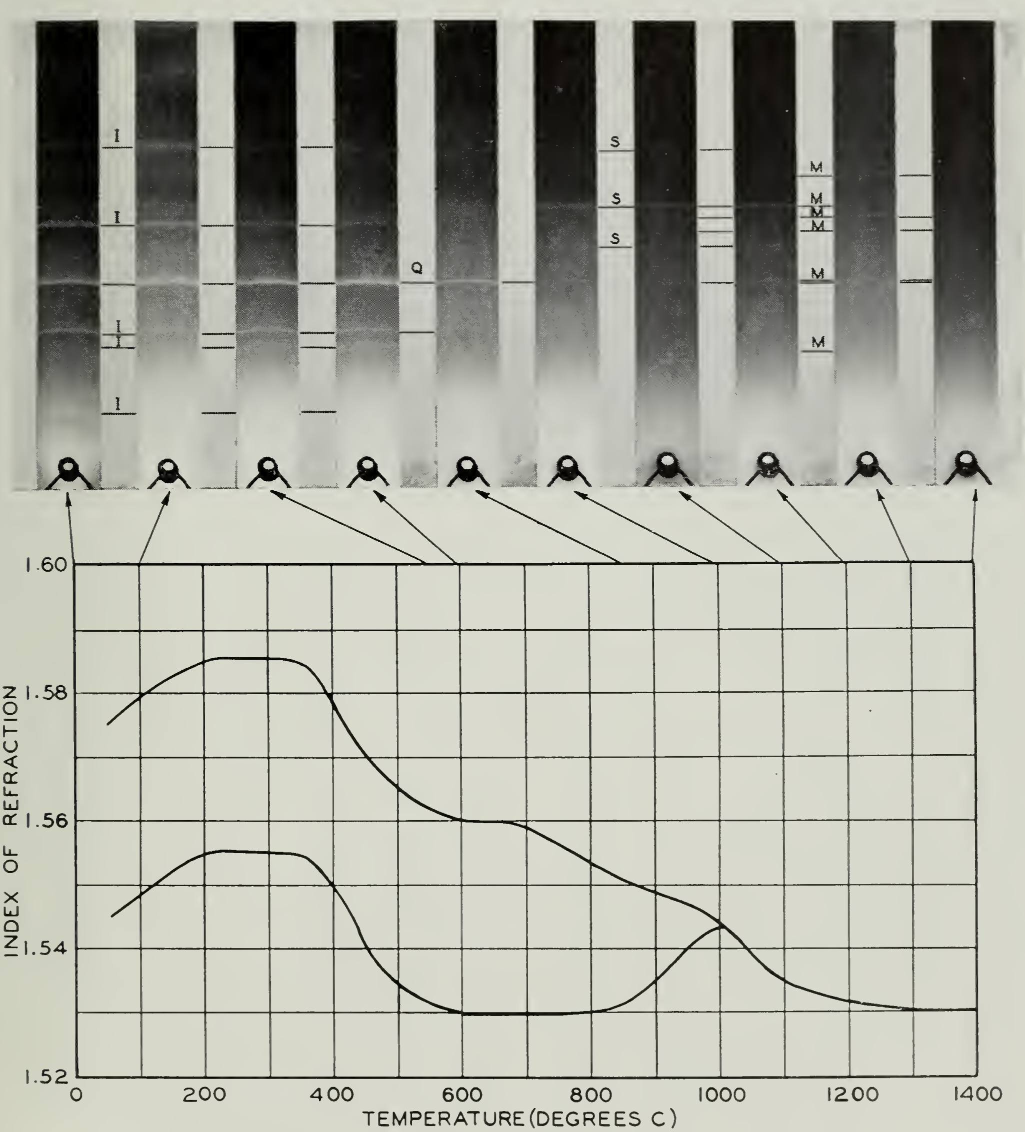

Fig. 1.—Indices of refraction and representative X-ray diffraction patterns of sample (1). The more prominent lines of various phases are designated as follows: I = illite, Q = quartz, S = spinel, and M = mullite.

which contained the largest amount of iron, also exhibited relatively greater vitrification at a lower temperature than the other illite samples.

Montmorillonite

The original samples of montmorillonite were light yellow-gray (No. 4) and light yellow (No. 5). At about 250°C., both samples became distinctly more yellow-red, and this color became darker on heating to successively higher temperatures. Both samples at 900°C. were light brown and showed no vitrification. At 950°C., they had the same color but had formed small powdery easily broken aggregates, thus showing the beginning of vitrification. At 1050°C., both samples were partially vitrified and slightly bloated; at 1200°C., vitrification was about complete. Sample (4) at 1300° and 1400°C. was brown glass with many large bloat holes. Sample (5) at 1300° and 1400°C. was steel-gray glass, not bloated.

CHANGES IN MINERAL COMPOSITION OF ILLITE ON FIRING

Interpretation of Optical Data

The indices of refraction for the three samples of illite, plotted in figures 1, 2, and 3, show such marked general similarity that it may be concluded that about the same changes took place in all samples of this clay mineral. There was little change in the general appearance of all three samples as observed under the microscope on heating up to about 800°C., and it was possible to measure γ and α values on all samples heated to this temperature. The birefringence, shown by the difference between the γ and α values, was retained in samples fired at 700°C. and then began to decrease slightly in samples fired at higher temperatures. Samples fired above 800°C. were unlike those fired at lower temperatures. Samples fired between 800°C. and 1000°C. had the appearance of a heterogeneous aggregation of unlike material, and it was possible only to approximate the spread of the indices of refraction.

The retention of the birefringence and of the original appearance to a temperature of 800°C. would indicate that the

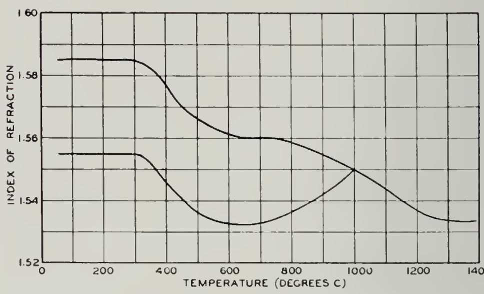

Fig. 2.—Indices of refraction of sample (2).

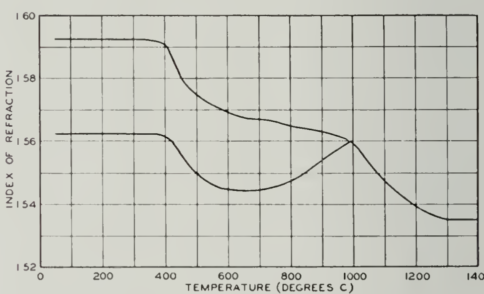

Fig. 3.—Indices of refraction of sample (3).

illite structure was not completely lost before this temperature was reached. The reduction in the birefringence at 700°C. suggests that the final destruction of the illite lattice begins at about this temperature.

Sample (1), the relatively low K_2O illite with high plastic and bonding properties, unlike samples (2) and (3) shows an initial increase in indices of refraction on firing up to 200°C. The explanation for this increase is not entirely clear, but it probably results from the finer ultimate particle size of this illite as compared to the other illite samples with the attendant greater difficulty in removing adsorbed water.

From 350° or 400° to 600°C., there is a decrease in indices of refraction corresponding to the loss of (OH) water from the lattice.[3] Between 600° and 700°C., there is little change in the indices of refraction or in the birefringence, suggesting a period of existence of the illite from which (OH) water has been completely lost prior to its final breakup.

[3]U. Hofmann and J. Endell, "Dependence of Base-Exchange and Swelling of Montmorillonite on Preheating." *Z. Ver. deut. Chem.*, Beihefte No. 35, 10 pp. (1939).

The optical data gave no indication of the composition of the material heated to 800° to 1100°C. other than to indicate a heterogeneous material that is changing continually with increasing temperatures.

Samples heated to 1100°C. show the presence of glass (the indices given on figures 1, 2, and 3 for samples heated to 1100°C. and above are for the glass component) through which are scattered many minute discrete particles that cannot be identified. Samples heated to 1300° and 1400°C. show needles of mullite disseminated through the glass.

Interpretation of X-Ray Data[4]

As might be inferred from the foregoing optical examination, the three illite specimens investigated exhibited parallel successions of phase changes, differing only in the apparent relative amounts and, to a small degree, in the temperatures at which new phases developed. Diffraction diagrams illustrating these changes are reproduced only for sample (1). The clay mineral persists in effect to about 850°C. in each sample. In agreement with the index curves, there are characteristic differences in the diffraction diagram before and after loss of (OH) water from the lattice. The positions of the 001 reflections are shifted slightly corresponding to an increase of 1 or 2% in the cell height, and the relative intensity of the 004 and 008 lines are noticeably greater for the dehydrated state. Above 600° to 700°C., the illite diffraction lines gradually disappear, being observed for the last time at 850°C. Small amounts of α-Fe_2O_3 have become apparent at 850°C., particularly in sample (3), but it seems probable that this iron constituted a limonite impurity in the original clays. The basic portion (MgO, Fe_2O_3, Al_2O_3) of the clay mineral gives rise, in this same temperature range, to the appearance of an entirely new phase, a spinel. The spinels comprise a highly variable group of cubic double (or mixed) oxides which have been the subject of extensive research.[5] The spinel developed in these three cases has a unit cube edge of about 8.15Å. and probably represents a composition $(Mg{\cdot}Fe)\ (Al_2{\cdot}Fe_2)O_4$. Both the amount present and the particle size of the phase increase with increased ignition temperature through 1100° or 1200°C. By 1300°C., however, the spinel in each case has dissolved in the glass. In each sample, mullite needles appear in varying amounts, first becoming apparent at around 1100°C. and persisting beyond the solution of the spinel. The amounts of spinel and of mullite appear to be complementary, and the richer spinel specimens are subject to fusion at the lower temperatures. A minor amount of quartz, from which it was impractical to completely free the illite samples examined, persisted without any inversion to cristobalite until its gradual solution between 850° and 1050°C.

The spinel and mullite phases above are of particular interest in comparison with the changes on firing of the crystalline micas. Muscovite[6] ignites to leucite and γ-Al_2O_3 and finally to α-Al_2O_3. A biotite examined by us yielded leucite, γ-Fe_2O_3, and a very little of a spinel similar to those mentioned before, around 1200°C., with γ-Fe_2O_3 remaining as a crystalline phase at 1350°C. These γ-oxide phases are, of course, themselves spinel-like phases, but have different characteristic cube-edge lengths.

Summary of Mineral Changes in Illite

Illite loses (OH) water from its lattice between about 350° and 600°C., retaining its essential micaceous character but assuming the form of a new "anhydrous modification." The final destruction of the illite lattice becomes complete around 800° to 850°C. The optical data suggest that the dehydrated lattice persists with little change between 600° and 700°C. and that following 700°C., the final destruction is gradual. The "anhydrous modification" exhibits a slightly larger unit cell height and distinctly lower refractive indices than does the normal mineral with its (OH) groups intact.

[4] X-ray diffraction diagrams were obtained in the laboratories of the Chemistry Department of the University of Illinois through the courtesy of G. L. Clark. All diffraction diagrams were registered with $FeK\alpha$ radiations in a camera of 6.33 cm. radius (reduced 35%).

[5] T. F. W. Barth and E. Posnjak, "Spinel Structures with and without Variate Atom Equipoints," *Z. Krist,* **82**, 325–41 (1932).

[6] A. Swetsch, "X-Ray Experiments in Ceramics," *Ber. deut. keram. Ges.*, **15**, 2–14 (1934).

At 850°C., a spinel, a new phase, appears, which increases in size of particle and in amount with temperatures up to 1100° or 1200°C. The middle sheet of the illite lattice, carrying the alumina, magnesia, and iron, seems to go into the formation of the spinel, and the alkalis and the silica from the outer sheets go into amorphous glass.

By 1300°C., the spinel has dissolved in the glass. Mullite becomes apparent at 1100°C. and persists to the final firing temperature employed in this work (1400°C.). A vitrified appearance at 950°C. suggests that glass formation has started at this temperature. The quartz present persists, without any inversion to cristobalite, until it is dissolved in the glass at about 1050°C.

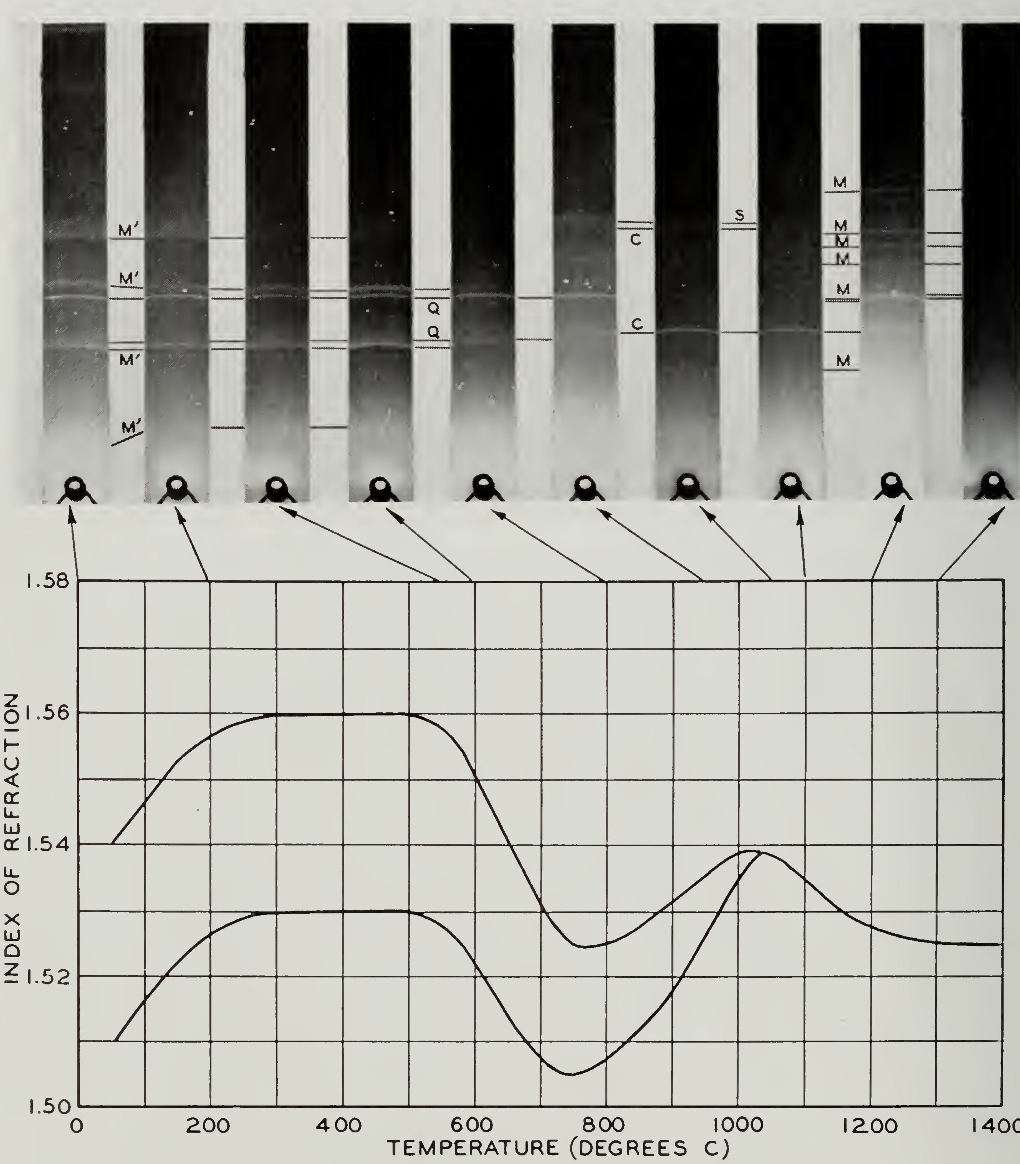

FIG. 4.—Indices of refraction and representative X-ray diffraction patterns of sample (4). The more prominent lines of various phases are designated as follows: M′=montmorillonite, Q=quartz, C = cristobalite, S=spinel, and M=mullite.

CHANGES IN MINERAL COMPOSITION OF MONTMORILLONITE ON FIRING

Interpretation of Optical Data

All of the fired samples of purified montmorillonite (No. 4), up to and including that fired at 800°C., retain the same appearance under the microscope and permit the determination of γ and α values (figure 4). The birefringence does not change at firing temperatures up to 600°C., but it gradually decreases as the firing temperature increases to 800°C. Samples heated above 800°C. show a rapid drop in the spread of the indices of refraction and a changed appearance under the microscope. It is suggested from these data that the final destruction of the montmorillonite lattice begins at about 600°C. and is essentially complete at about 800°C.

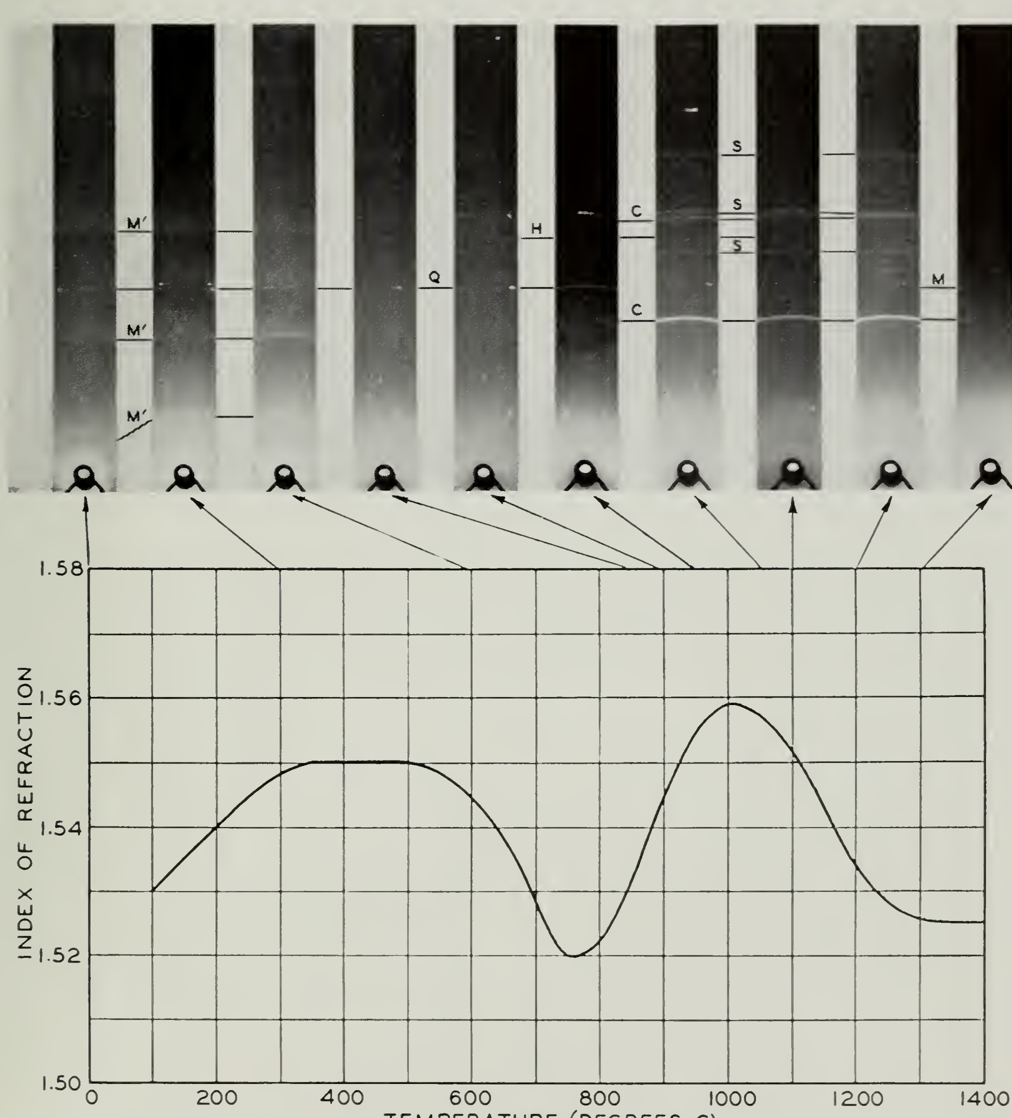

Fig. 5.—Indices of refraction and representative X-ray diffraction patterns of sample (5). The prominent lines of various phases are designated as follows: M′=montmorillonite, Q=quartz, H=hematite, C = cristobalite, S=spinel, and M=mullite.

The indices of refraction increase as the temperatures of firing increase up to about 300°C. As for illite sample (1), it is suggested that this results from the slow loss of adsorbed water because of the very small ultimate particle size of the clay mineral. There is no change in the birefringence or decrease in the indices of refraction at firing temperatures up to 500°C. Above 500°C., the indices of refraction decrease, and above 600°C., the birefringence also decreases. This suggests that the (OH) water of the lattice begins to come off by 500°C. and is followed by the final destruction of the lattice. Like illite, an "anhydrous modification" develops with the loss of (OH) water from the lattice, but the temperature interval in which it is stable is much shorter than that for illite.

Only the range of indices of refraction can be measured on samples heated to temperatures between 800° and 1050°C. The components existing in this temperature range cannot be identified optically, and the optical data merely suggest that a heterogeneous changing mixture of components exists.

The sample fired at 1050°C. showed glass (the indices of samples fired to temperatures above 1050°C. on figure 4 are those of the glass) through which many discrete unidentified particles are scattered. Samples fired to higher temperatures showed successively more glass, and samples fired at 1300° and 1400°C. were largely glass with scattered needles of mullite.

Only a mean index of refraction could be measured for the fired samples of the impure montmorillonite, sample (5), and these data are given in figure 5. These optical data are too limited to be very significant, but the fact that the values for this sample run about parallel with those of sample (4) suggest that the changes in sample (5) were about the same as those that took place in sample (4).

[7](*a*) G. Nagelschmidt, "Lattice Shrinkage and Structure of Montmorillonite," *Z. Krist.*, **93** [6] 481–87 (1936); *Ceram. Abs.*, **15** [8] 258 (1936).

(*b*) W. F. Bradley, R. E. Grim, and G. L. Clark, "Behavior of Montmorillonite on Wetting," *Z. Krist.*, **97**, 216–22 (1937); *Ceram. Abs.*, **17** [8] 288 (1938).

(*c*) E. Maegdefrau and U. Hofmann, "Crystal Structure of Montmorillonite," *Z. Krist.*, **98**, 299–323 (1937); *Ceram. Abs.*, **18** [2] 58 (1939).

(*d*) See footnote 3.

Interpretation of X-Ray Data

The two montmorillonite specimens investigated differed more from each other than did the illite samples among themselves, but, on the whole, they also exhibited similar successions of phase changes. Numerous investigations[7] of the behavior of montmorillonite toward low-temperature water have been reported and no attention has been given to this problem here. Interest is directed only to the water-free pyrophyllitelike product from which hydration water has been irreversibly lost. This material is first observed around 200° to 300°C. as a triple layer structure quite analogous to the micas, and, as in the case of the illites, an increase in the unit-cell height of about 1% is observable by about 600°C., which it is assumed relates to the loss of (OH) water from the actual lattice. This phase, again, might be spoken of as a new "anhydrous modification" of the normal mineral.

The rather pure specimen (No. 4) exhibited lines of this "anhydrous modification", which persisted to about 800°C. By 850°C., the montmorillonite is rather completely decomposed, and a spinel phase has appeared. For this specimen, which contains little iron, the phase is apparently spinel itself, the cube length being 8.05 Å., and the estimated amount of the phase developed is the least for the five samples studied. The crystallization of the raw unpurified bentonite (No. 5) was distinctly less perfect to start with, and clay lines easily discerned persisted only to about 600°C. Little more can be observed until around 850° to 900°C., where both α-Fe_2O_3 and a spinel phase become apparent. The α-Fe_2O_3 appears first, suggesting that it develops from the limonite impurity known to be present rather than from the clay mineral. Between 1050° and 1200°C., the amount of α-Fe_2O_3 decreases, whereas the cube-edge length of the spinel grows from about 8.1 to 8.2 Å., evidently by dissolution of the α-Fe_2O_3.

The spinels in each case grow and become more abundant and then fuse into the glass, just as in the case of the illites. Mullite appears, as before, around 1050° or 1100°C., and the mullite-spinel propor-

tions appear complementary; that is, No. 4 develops very little spinel and abundant mullite, whereas No. 5 develops abundant spinel and only a few mullite needles. Each of the montmorillonite samples precipitates considerable crystalline silica at about 950°C. In the case of sample No. 4, contaminated with very fine-grained quartz, it is not certain whether the newly synthesized silica is quartz or cristobalite, for inversion is taking place in the same range. In sample No. 5, however, it is distinctly apparent that quartz precipitates as such and that it later inverts to cristobalite. In each case, the cristobalite fuses with the glass at about the same temperature as the spinel.

Summary of Mineral Changes in Montmorillonite

Final destruction of the montmorillonite lattice begins at about 600°C., immediately following the loss of (OH) lattice water, and is essentially complete at 800° to 850°C. The loss of (OH) water is first reflected in the optical values at about 500°C. by a reduction in the indices of refraction. A slight increase (about 1%) in the height of the unit cell also accompanies the loss of the (OH) water.

A new phase, spinel, appears at 850°C. and increases in particle size and abundance up to temperatures of about 1100°C. By 1300°C., all the spinel is dissolved in the glass. Mullite appears at about 1050°C. and increases in abundance with higher firing temperatures. As in the case of illite, it appears that the middle sheet of the montmorillonite lattice, carrying alumina, iron, and magnesia, goes to form spinel. A considerable portion of the silica of the outer sheets, however, contributes synthetic crystalline silica, and the remainder combines with the alkalis to form glass. The formation of amorphous glass, the development of crystalline silica, and the beginning of vitrification are first evident at about 950°C. In sample No. 5, it is clear that the crystalline silica is first quartz, which later inverts to cristobalite. The cristobalite is dissolved in the glass by 1300°C.